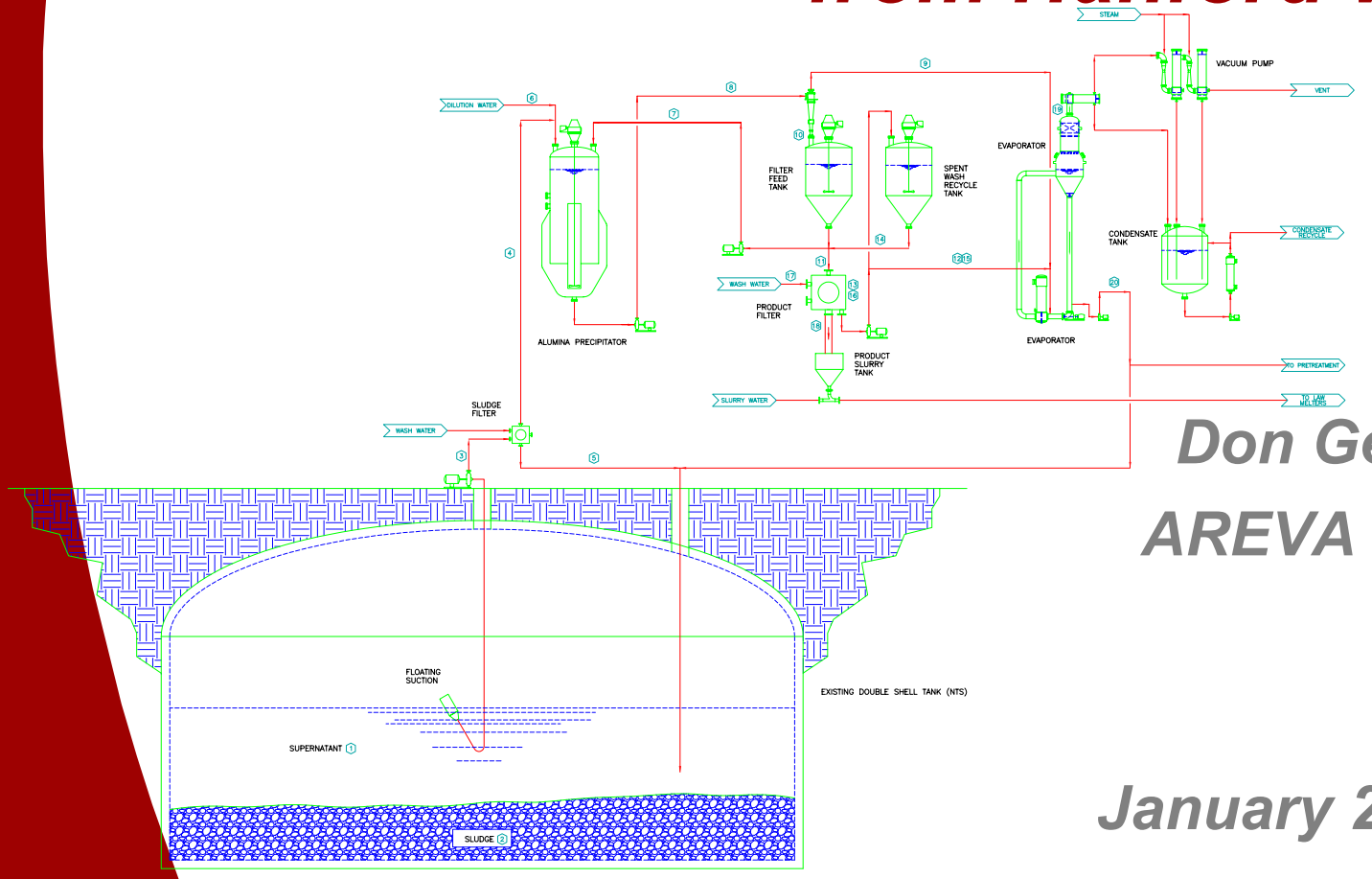
Modified Bayer Process for Alumina Removal from Hanford Waste



Don Geniesse

AREVA NC Inc.

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Alumina Removal Team

- ***AREVA NC - Don Geniesse, Eric Nelson, Gary Stegen***
- ***Penn State - Dr. Tony Perotta***
- ***RJ Lee - Randy Hermann, Marisol Avila***

Hanford Alumina Problem

Current Waste Na	44,000 MT
Additional Na to Leach Al	30,000 MT
Total Na to WTP	74,000 MT

- Additional Na needed to leach Al sludge increases WTP Na by 68%
- Additional Na increases WTP glass volume and treatment schedule proportionally
- Soluble Al can plug WTP equipment by forming amorphous gel during filtration, ion exchange, cooling, dilution, and/or neutralization operations in WTP

Alumina Solubility

- ***Alumina solubility is highly temperature dependent***

  $$Al(OH)_{3(s)} + OH^{-1} \rightarrow Al(OH)_4^{-1}$$

- ***Alumina has poor solubility at 25ºC***

  $$Al(OH)_{3(s)} + 5NaOH \rightarrow Al(OH)_4^{-1} + Na^{+1} + 4NaOH$$

  ~4 moles excess NaOH required to maintain 1 mole $Al(OH)_4^{-1}$ soluble at 25ºC

- ***Alumina has enhanced solubility at 100ºC***

  $$Al(OH)_{3(s)} + 2NaOH \rightarrow Al(OH)_4^{-1} + Na^{+1} + 1NaOH$$

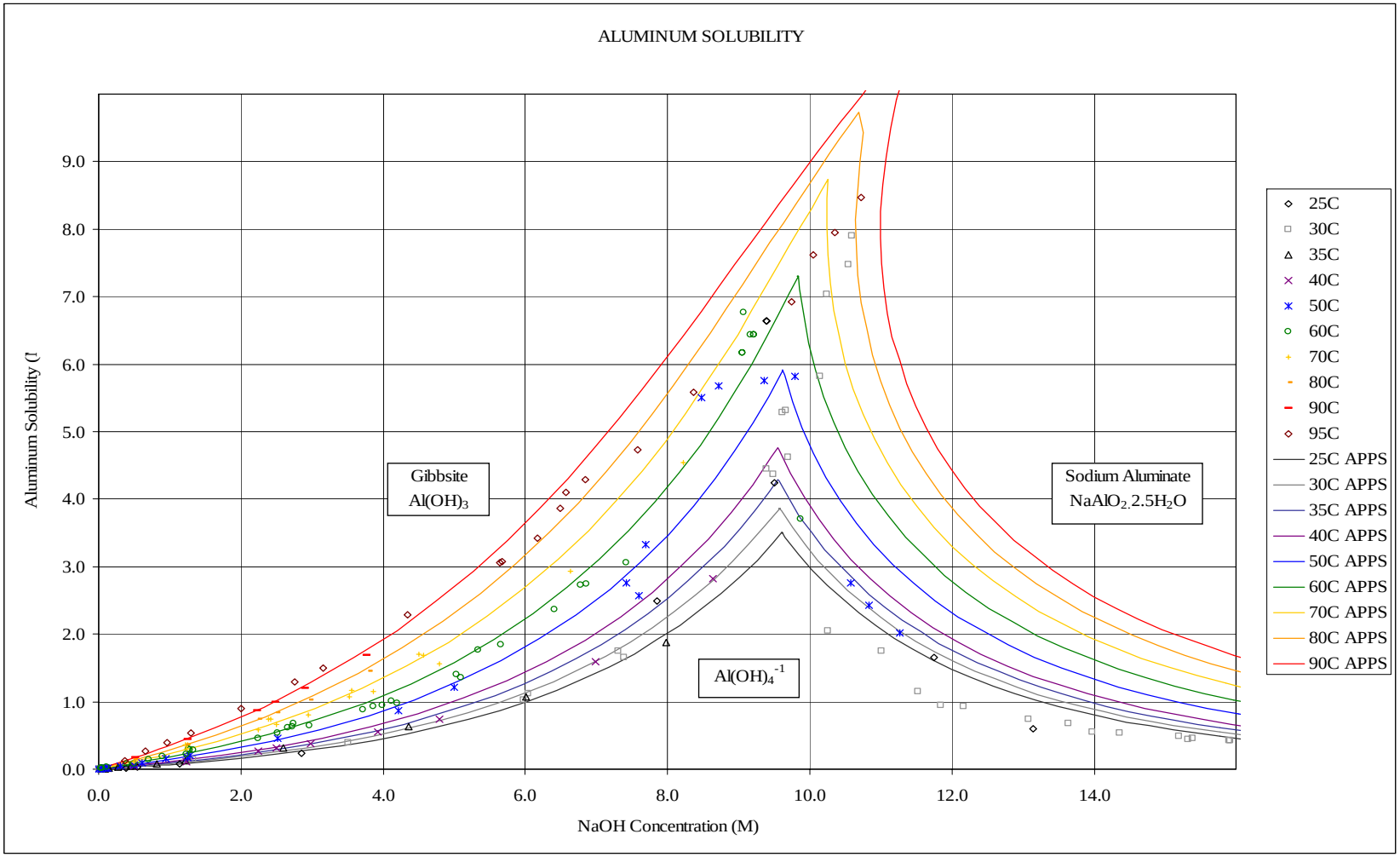
  ~1 mole excess NaOH is required to maintain 1 mole $Al(OH)_4^{-1}$ soluble at 100ºC

- ***Precipitation of gibbsite regenerates hydroxide***

  $$Al(OH)_4^{-1} \rightarrow Al(OH)_{3(s)} + OH^{-1}$$

- ***Elevated temperature leaching and cooling precipitation regenerates hydroxide for additional leaching – reducing or eliminating NaOH demand for leaching alumina***

Gibbsite Solubility



Gibbsite Solubility is Strongly Dependent on Temperature

Modified Bayer Process

- *Conventional method used by aluminum industry leaches alumina from bauxite @ 150ºC & precipitates gibbsite @ 60ºC in seeded solution*
- *Proposed Modified Bayer Process leaches alumina sludge at 100ºC and precipitates clean, crystalline gibbsite at 60ºC*
- *Bayer process regenerates hydroxide for additional alumina leaching*
- *Clean, precipitated gibbsite may be used as a WTP glass former, reducing total glass volume by offsetting imported glass formers*

Modified Bayer Process Experiments
DST Simulant Tests

Leach At 100ºC - Seed, and Precipitate $Al(OH)_3$ at 60ºC

Filter and Wash Precipitate

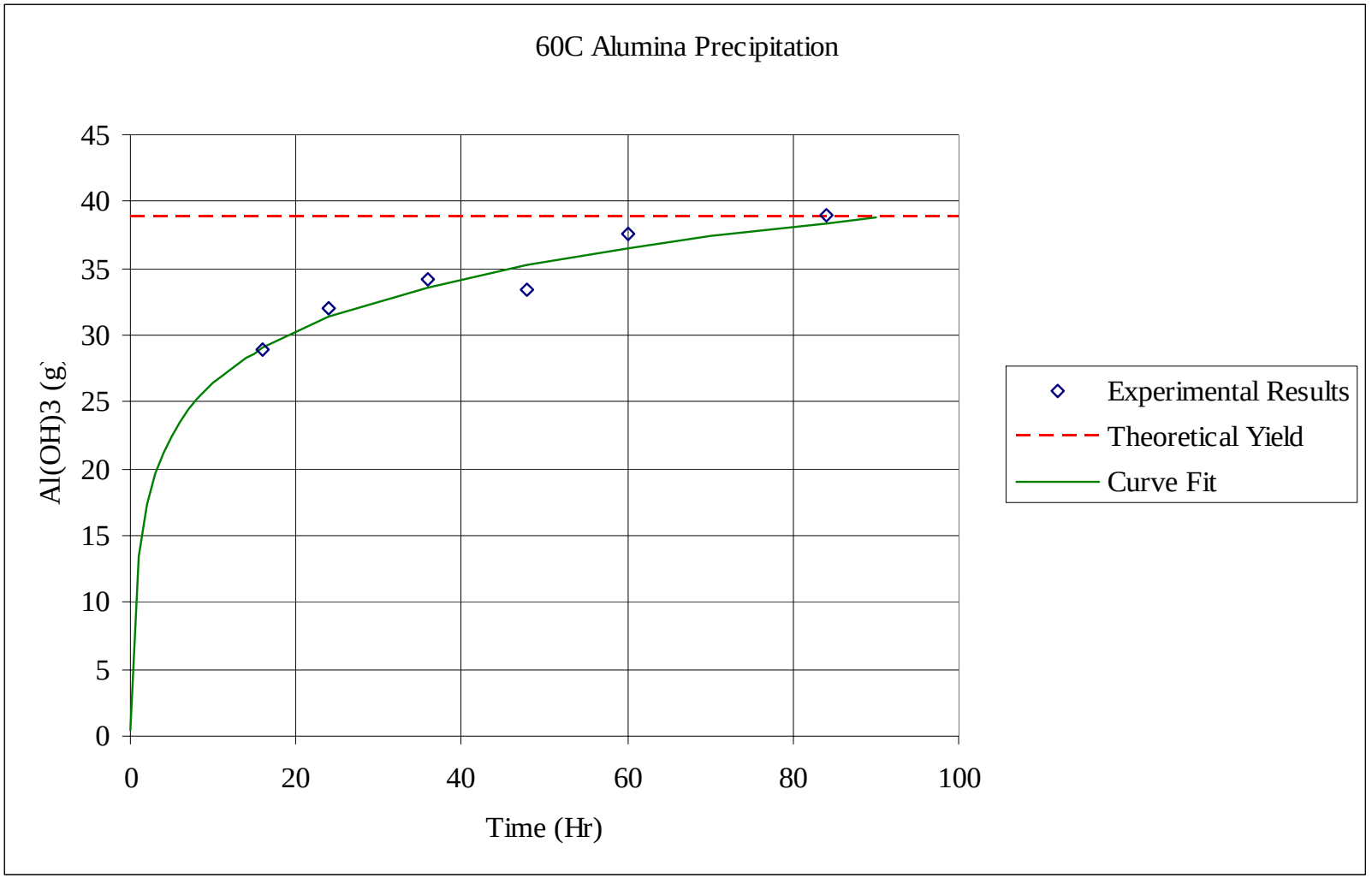
Precipitation Methods

- ***Cooling Precipitation - for regenerating NaOH and recycling leachate solution***
- ***Dilution Precipitation - improved yield for regenerating NaOH & recycling leachate***
- ***Partial Neutralization – precipitates nearly all alumina for one-pass operation (no leachate recycle)***
- ***Lithium Alumina Carbonate Precipitation–***

$$4Al(OH)_4^{-1} + Li_2CO_3 + 3H_2O \rightarrow Li_2CO_3.4Al(OH)_3.3H_2O + 4OH^{-1}$$

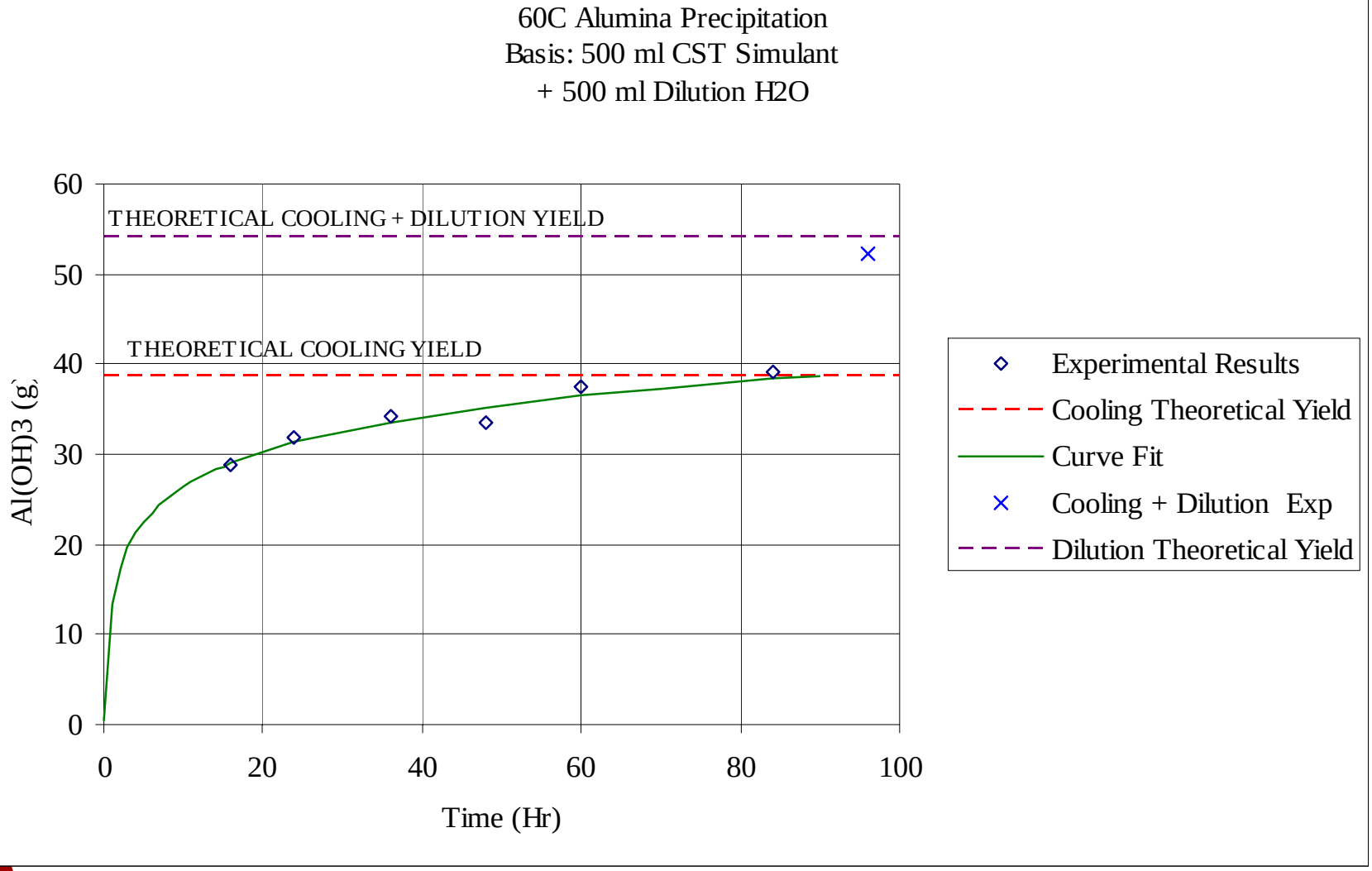
Removes nearly all alumina and allows recycle of strong leachate solution

60ºC Cooling Gibbsite Precipitation



75% of Theoretical Yield in 24 Hours
~100% in 4 days

60ºC Cooling & Dilution Gibbsite Precipitation

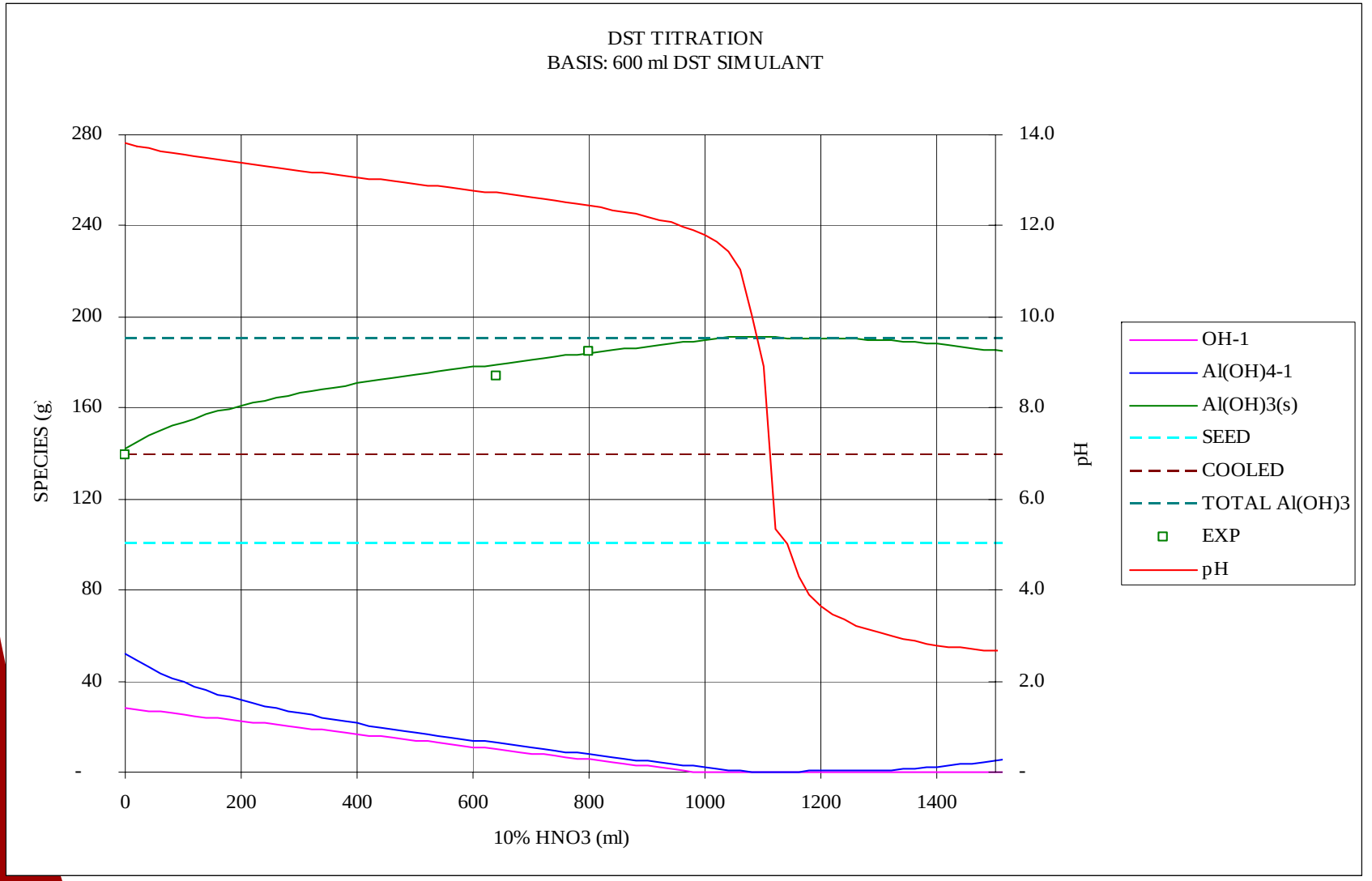


Single Pass Yield Improved 40% by 1:1 Dilution

Partial Neutralization Gibbsite Precipitation

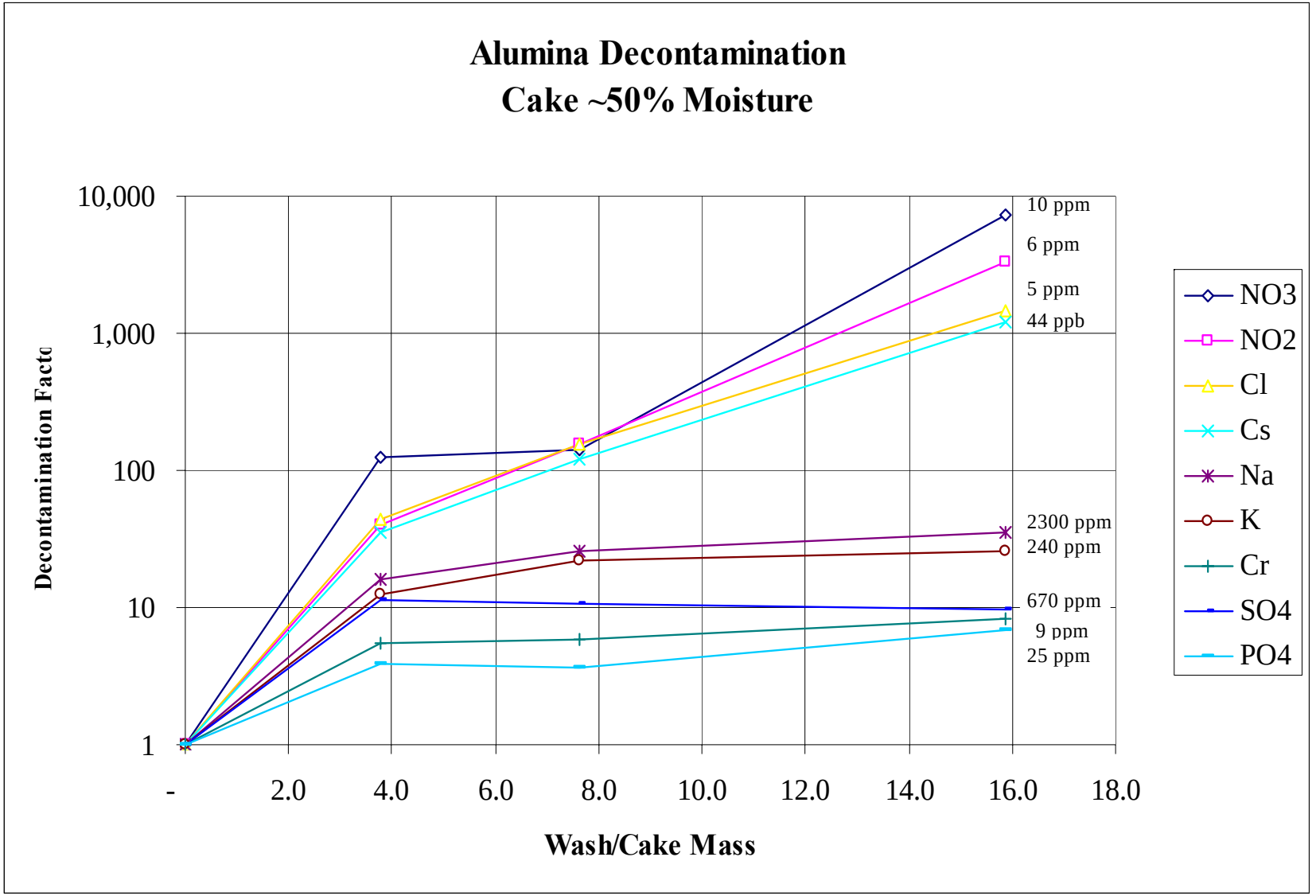
- *Partial Neutralization precipitates soluble alumina from supernatants to prevent downstream plugging (60ºC supernatants can gel when cooled to 25ºC)*
- *Partial neutralization done under same conditions as cooling precipitation (60ºC & seeded)*
- *Supernatant neutralized with 10% HNO_3 to pH endpoint of 11*

Partial Neutralization $Al(OH)_3$ Precipitation



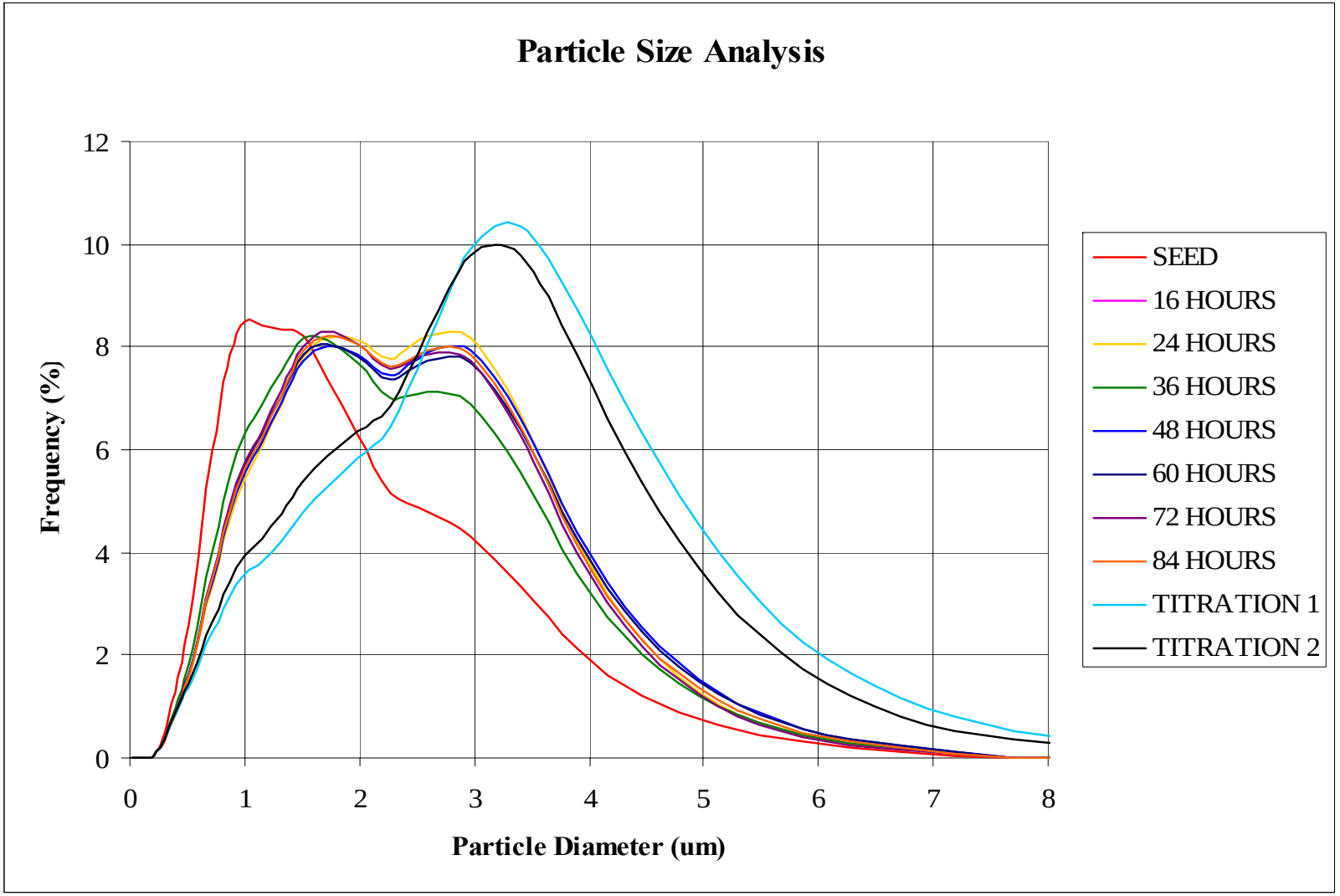
96% of Total Alumina Removed by Partial Neutralization

Product Cake Decontamination



Product Easily Filtered - 99.7% $Al(OH)_3$ Purity
Cs Removed in Proportion to Wash Ratio

Gibbsite Crystal Size



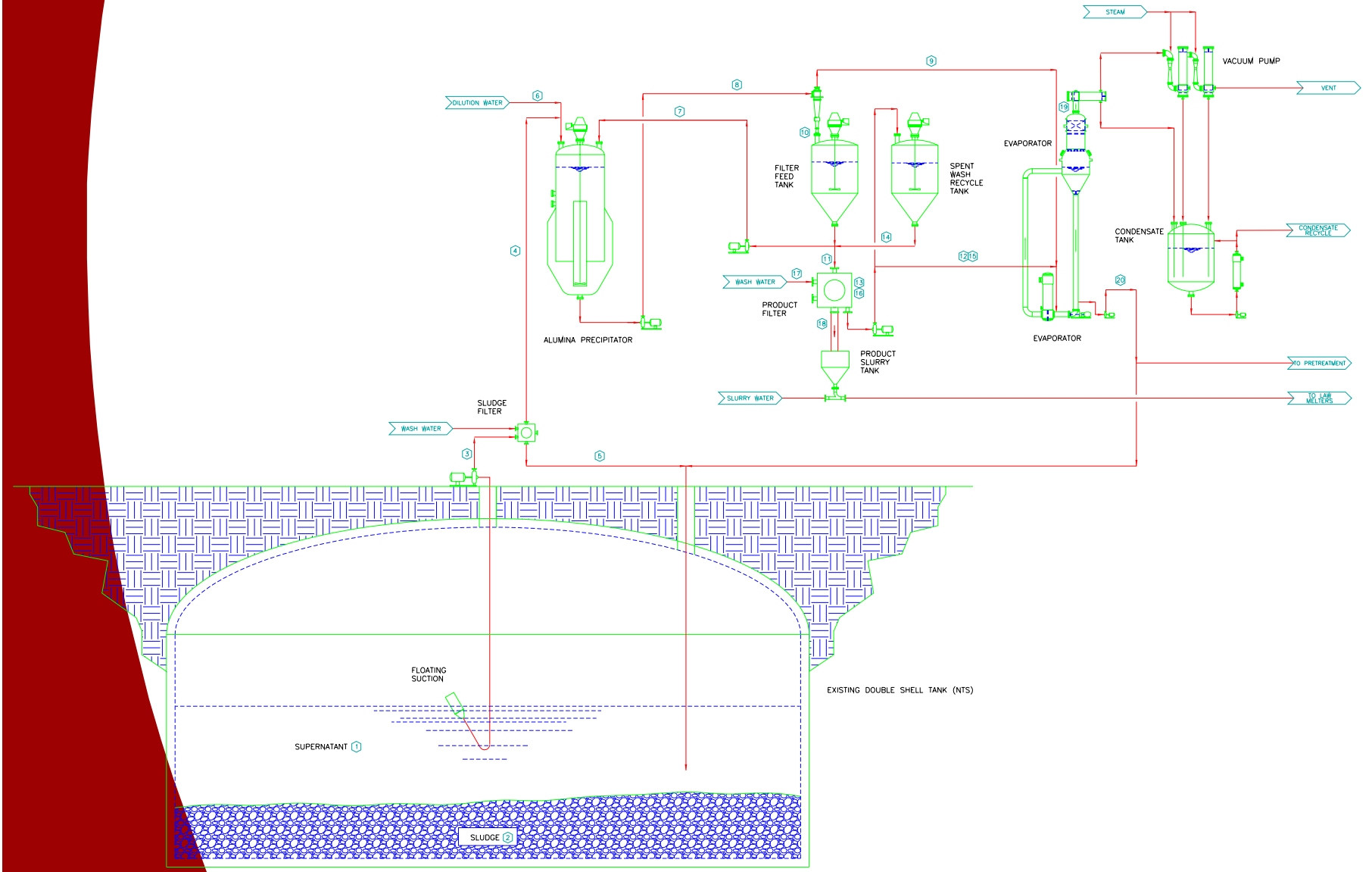
Precipitation Occurs by Seed Growth

Hanford Application of Modified Bayer Process

1. Leach alumina sludge in-situ from tank sludge, decant supernatant & precipitate alumina as clean gibbsite by Modified Bayer Process
2. Precipitated gibbsite is decontaminated with wash water to remove interstitial (Cs, Tc, I) contamination
3. Evaporate filtrate to re-constitute leach liquor & recycle
4. Partially neutralize supernatants to precipitate gibbsite from WTP feed
5. Use recovered, decontaminated $Al(OH)_3$ as glass former in WTP melters

Modified Bayer Process

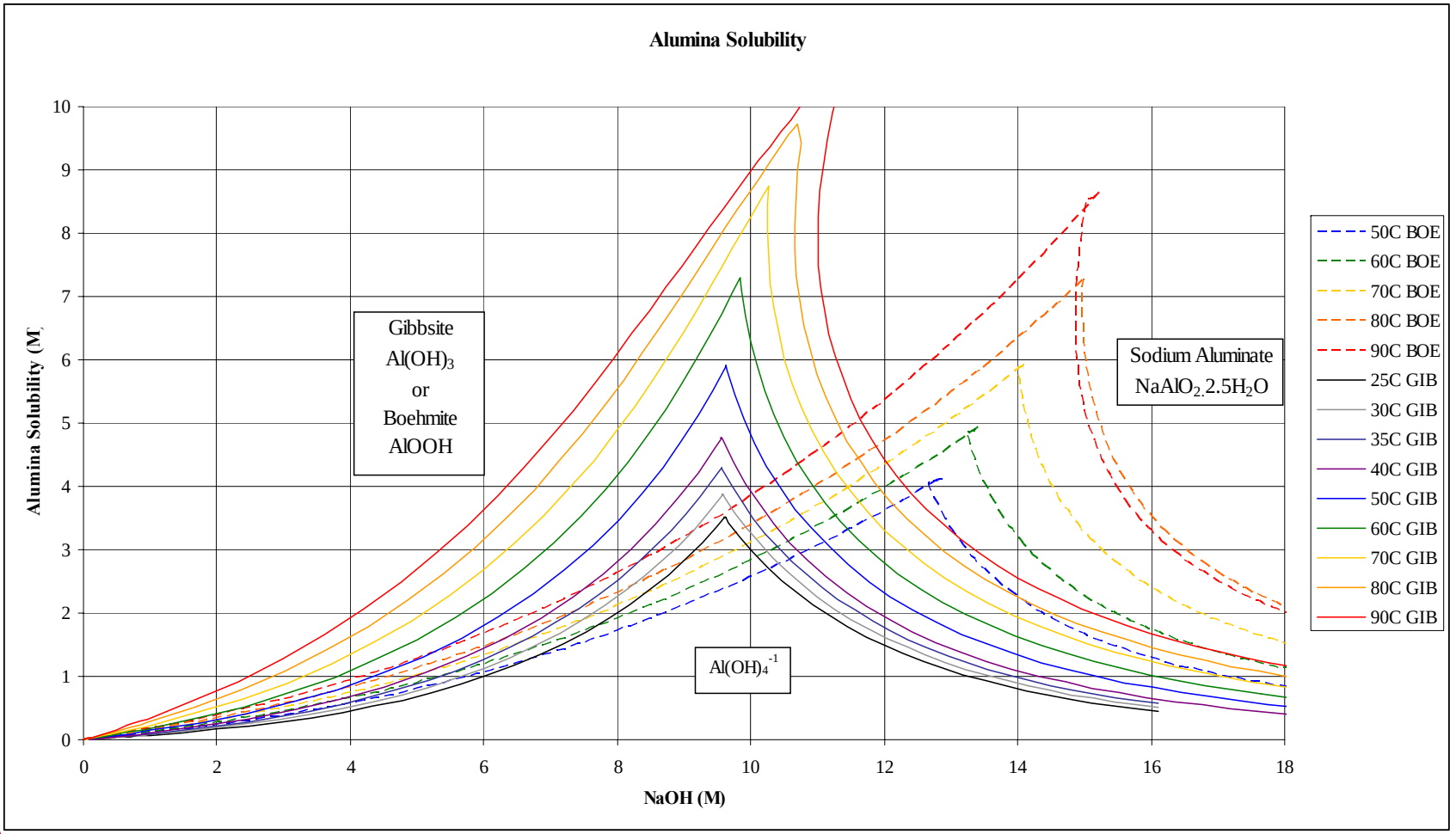
Preliminary Process Flow Diagram



Pneumapress® Filter

Simple, Contained Filter Press

Boehmite (AlOOH) Solubility



Boehmite is more stable & less soluble than gibbsite

Summary

- ***Modified Bayer Process is a simple and effective method for removing and decontaminating soluble alumina and gibbsite sludge from Hanford Waste***
- ***Existing equipment (DSTs, evaporators) may be used to reduce capital cost***
- ***Process may be enhanced by dilution, partial neutralization, or lithium alumina carbonate precipitation to pre-condition liquor for WTP feed***
- ***Boehmite removal requires more robust leaching and/or precipitation conditions than gibbsite***

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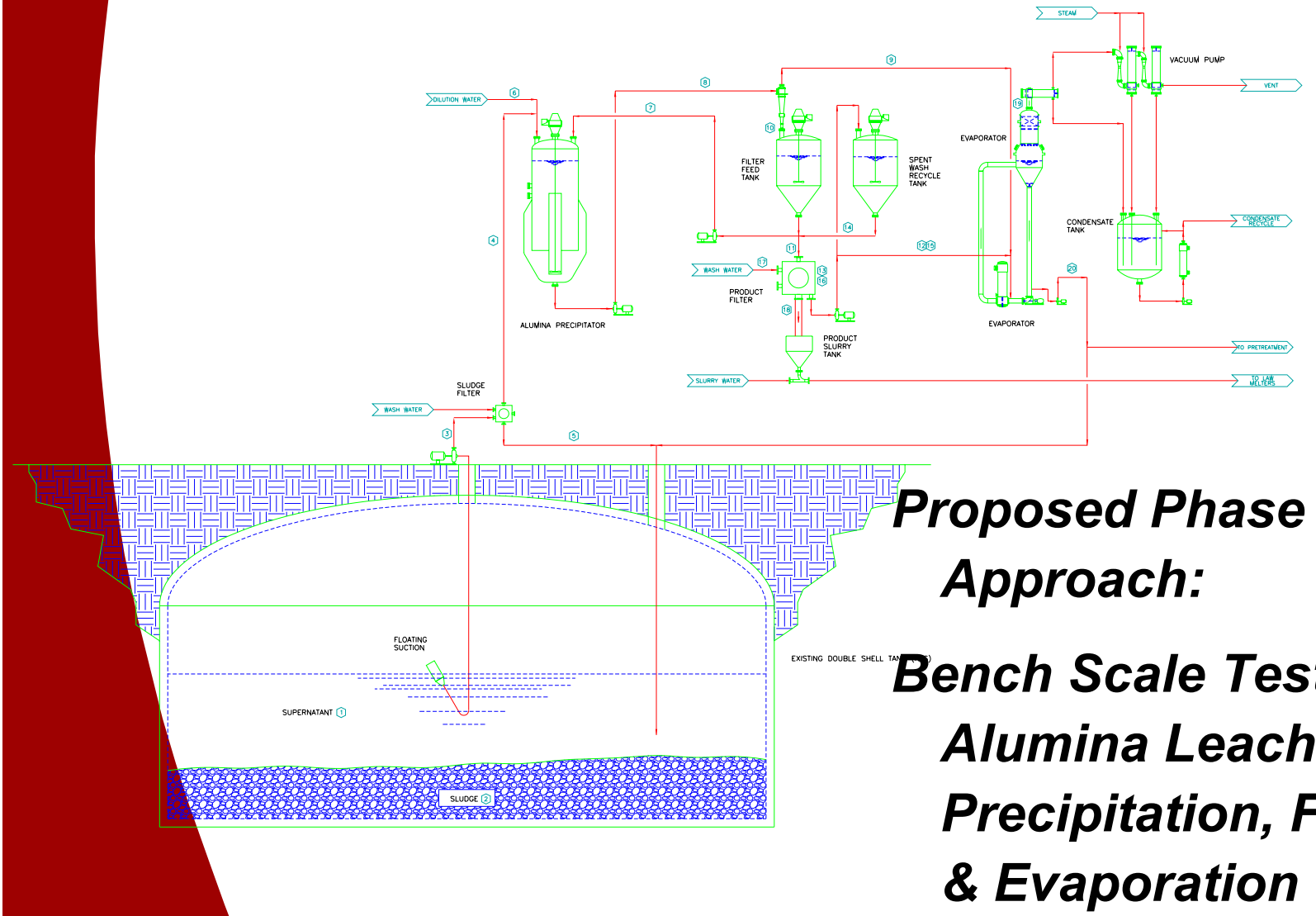


Proposed Phase 2 Approach:

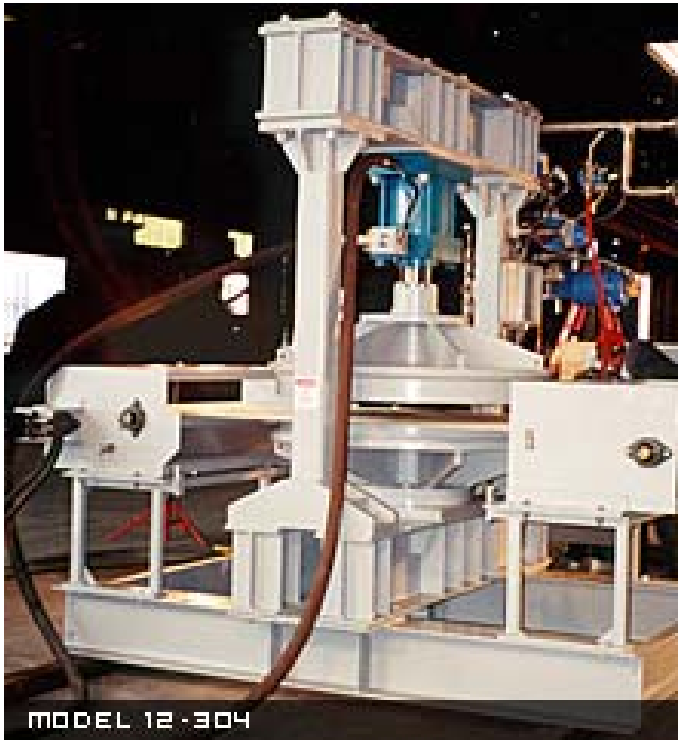
Bench Scale Testing of Alumina Leaching, Precipitation, Filtration, & Evaporation

Phase 2 Bench Tests
10 Liter Scale

- Gibbsite & Boehmite Leaching from Simulated Sludge
- Seeded Gibbsite Precipitation
- Pressure Filtration/Wash Testing
- Seed Recycle
- Evaporation & Recycle of Filtrate

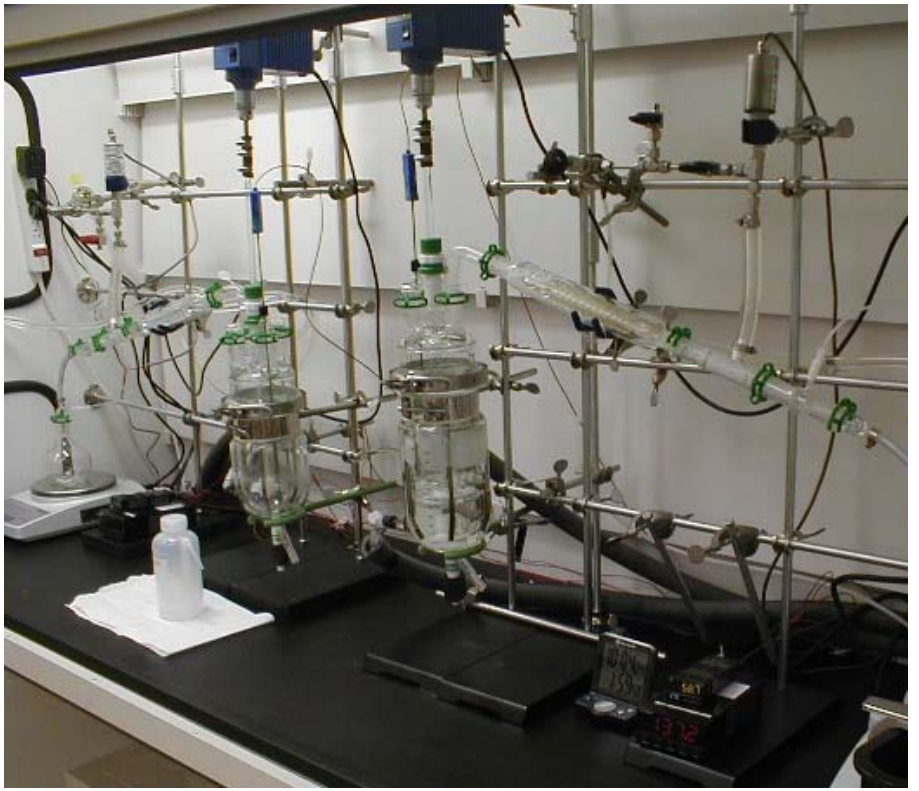
Phase 2 Pilot Tests
500 gallon Scale

- *Vendor Tests will use Simulated Waste/C-31 Seed Slurry*
- *Tests will determine Capacity of Full-Scale System using 5 gpm pilot unit*
- *Full-scale Wash/Cake Decontamination Factors*
- *Cake Handling Properties*



Phase 2 Laboratory Tests
1 Liter Scale

- *Boehmite Leaching/Gibbsite Precipitation*
- *Lithium Alumina Carbonate Crystallization*
- *Effects of Organic Contaminants*
- *Alternate Waste Compositions*



Phase 2
Future Work Summary

Phase 2 Work will Optimize Process Parameters for Design of Full-scale System and Specify Conditions for Hot Work Testing

- ***Precipitation Residence time***
- ***Amount of Seed and Extent of Seed Recycle***
- ***Amount of Wash and Extent of Decontamination***
- ***Evaporation & Recycle of Filtrate for Leaching***
- ***Potential Application of Lithium Alumina Carbonate***
- ***Boehmite Leaching***
- ***Alternate Waste Composition & Effects of Organics***